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Research Article

Silica-Supported Co_3O_4 Nanoparticles as a Recyclable Catalyst for Rapid Degradation of Azodye

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Abstract

In this paper, silica nanoparticles with particle size of ~ 10-20 nm were selected as a support for the synthesis of Co_3O_4 nanoparticles by impregnation of silica nanoparticles in solution of Co(II) in a specific concentrations and then calcination to 800 °C. This nanocomposite was then, used as a catalyst for oxidative degradation of methyl orange (MO) with ammonium persulfate in aqueous media. Effect of pH, temperature, contact time, amount of oxidant and catalyst were studied in the presence of manuscript. Scanning electron microscope (SEM), electron dispersive spectroscopy (EDS), FT-IR, and ICP-AES analyses were used for analysis of silica-supported Co_3O_4 (Co_3O_4/SiO_2). Treating MO with ammonium persulfate in the presence of Co_3O_4/SiO_2 led to complete degradation of MO under the optimized conditions. Also, the catalyst exhibited recyclability at least over 10 consecutive runs.

Keywords: Co_3O_4/SiO_2; oxidative degradation; methyl orange; catalytic oxidation

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1. Introduction

Production of wastewater from various industries is a critical threat to pollute air, seawater, groundwater, etc. [1-4]. Therefore, the treating such wastewaters followed by recycling is a big opportunity to decrease both pollution and makes possible to recycle the water in the same industry [1]. For instance, in textile industry, there is a major concern in treating the wastewater and recycling of the treated water [4,5]. Advanced oxidation processes (AOP), such as: Fenton's reaction and photodegradation methods have been practical approaches for degradation of organic pollutants [6,7]. In Fenton's method, the mixture of H_2O_2 and Fe(II) electrochemically produce and can regenerated throughout the process [8]. Treating with H_2O_2 is more preferable due to the fact that its use doesn't produce harmful side products [9]. However, there are some drawbacks which have made it hard to apply. Some of them include, higher Fe-based sludge production which needs to be mineralized, pH limita-

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tion (in the ranges of 2.5-3.5), using a higher amount of Fe(II), instability of hydrogen peroxide, and restriction in mineralization. Besides, sulfate radical can act as a suitable replacement to eliminate these restrictions in a way that they can sometimes degrades most of the organic pollutants [10]. Generation of sulfate radicals in the presence of a transition metal in a heterogeneous model can be reinforced and accelerated and also can be assumed as AOP [11]. Among the transition metals, Co^{2+} can be a good candidate for sulfate radical to accelerate the AOP [12,13]. On the other hand, we can support Co^{2+} on a heterogeneous surface like silica, titania, carbonaceous materials, etc. in the form of Co_3O_4 nanocrystalline [11,14-17]. Dionysiou and coworkers [18] studied supporting Co_3O_4 on silica and found it as a promising agent for AOP in the degradation of 2,4-dichlorophenol under UV light. That study showed that silica supported cobalt oxide can act as a robust catalyst in degradation area. Hence, in this paper, we studied another aspect of the catalytic degradation capability of silica-supported Co_3O_4 (Co_3O_4/SiO_2) in degradation of methyl orange (MO) in the presence of peroxydisulfate (PDS) on the basis of oxidative degradation by Co/PDS. This investigation indicated that Co_3O_4/SiO_2 can act catalytically in the degradation of MO in a few minutes in the presence of PDS as an oxidant. The Co_3O_4/SiO_2 also showed good recyclability at least for 15 runs and good applicability in wide range of pH values.

2. Materials and Methods

2.1. Instruments and apparatus

Silica nanoparticles (99.5%) with size of 10-20 nm (BET) and $CoCl_2.6H_2O$ (98%) were purchased from Sigma-Aldrich. Potassium persulfate (≥ 99.0 %) and MO (≥ 99.5%) were also purchased from Merck and used without further purification. Scanning electron microscope (SEM) images and electron dispersive analysis (EDS) were recorded on TESCAN Vega Model. X-ray diffraction (2θ range was 15-80) was performed by X-ray diffractometer, Bruker AXS-D8 Advance.

2.2. Synthesis of Co_3O_4/SiO_2

Synthesis of silica supported cobalt oxides was performed by impregnation method according to literature [19] with a slight modification on the procedure. A desired amount of cobalt(II) chloride hexahydrate in aqueous solution was added to silica nanopowder to obtain a certain amount of 25 wt% (based on the atomic absorption spectroscopy (AAS) reports) and allowed to stir for 2 h at room temperature. Then the solvent was evaporated by vacuum rotary. Then the obtained pinkish solid was transferred to furnace for calcination and the temperature was set to 800 ^oC for 6 h.

2.3. Degradation tests

All degradation tests were performed in 100 mL glass balloon. PDS source was supplied by potassium persulfate with various amount of concentrations in which the optimum amount was 0.04 mmol/L. For all tests, the concentration of MO was 10 ppm (20 mL in each degradation test). In the recycling tests, after the completion of the degradation, the catalyst was separated from reaction mixture by centrifuge and washed with distilled water and ethanol. Due to the very lower particle sizes of the catalyst, a very small part of the catalyst was indispensably lost in every cycle. For this reason, the scale of recycling test was increased 5 times.

3. Results and Discussion

3.1. Characterization of the catalyst

As mentioned, the synthesis of Co_3O_4/SiO_2 was performed by impregnation method at room temperature by dispersing silica nanoparticles in Co(II) solution. In this manner, Co(II) ions were adsorbed on the surface of silica and in the next step, it underwent calcination at 800 ^oC at air condition. Under the calcination, Co(II) ions were converted to cobalt oxide in the form of both Co(II) and Co(III) in Co_3O_4 crystalline structure. Figure 1 indicates the total pathway towards synthesis of Co_3O_4/SiO_2.

SEM images from Co_3O_4/SiO_2 indicates its morphology which is nanoparticles with uniform morphology (Figure 3). Particles size analyser (PSA) indicates the average size of the particles in 43 nm. EDS analysis indicated 27.5 wt% of Co which was supported on the surface of silica (Figure 2). In comparison, ICP-AES showed 25 wt% of supported Co which confirms the obtained data with a small difference. One speculation and rational reason for the high loading of Co on silica can be attributed to smaller particle sizes of silica nanoparticles (~10-20 nm). Therefore, smaller particle size causes a higher surface area available for Co loading.

X-ray diffraction pattern was also performed for analysis of crystalline behavior of Co_3O_4/SiO_2. To obtain the acceptable peaks relating to Co_3O_4, calcination temperature is an important factor, so in this regard, we set the temperature at 800 °C which was based on the previously reported literatures (Figure 4) [20]. As can be seen in Figure 4, some characteristic peaks in 2θ values of 30, 37, 44, 58, 59, and 63 can be attributed to this crystalline structure [19]. A broad band below 30 is also related to amorphous structure of silica [21,22].

3.2. Oxidative degradation of MO

For the catalytic tests of Co_3O_4/SiO_2, we first selected MO solution as a pollutant with the concentration of 10 ppm. The oxidant was selected from the family of sulfate radical producing agents, namely PDS. Before going to any further studies on the catalytic behaviour of Co_3O_4/SiO_2 in degradation MO, we made sure whether the removal of azodye is physically adsorpted or oxidatively degraded. For this query, we studied the effect of the PDS on the removal of MO. In the absence of PDS, the oxidant, there was only an insignificant fraction of MO removal which can be attributed to adsorption. The effect of catalyst amount was monitored to find an optimized ratio of Co_3O_4/SiO_2 to volume of MO solution. Accordingly, this ratio was 0.05 g of Co_3O_4/SiO_2 (Figure 5).

The concentration of PDS was also investigated on the degradation of MO when 0.05 g of Co_3O_4/SiO_2 was used in the degradation at room temperature. Therefore, by increasing the amount of PDS, the degradation of MO was also enhanced. In 1 mmol/L concentration, the

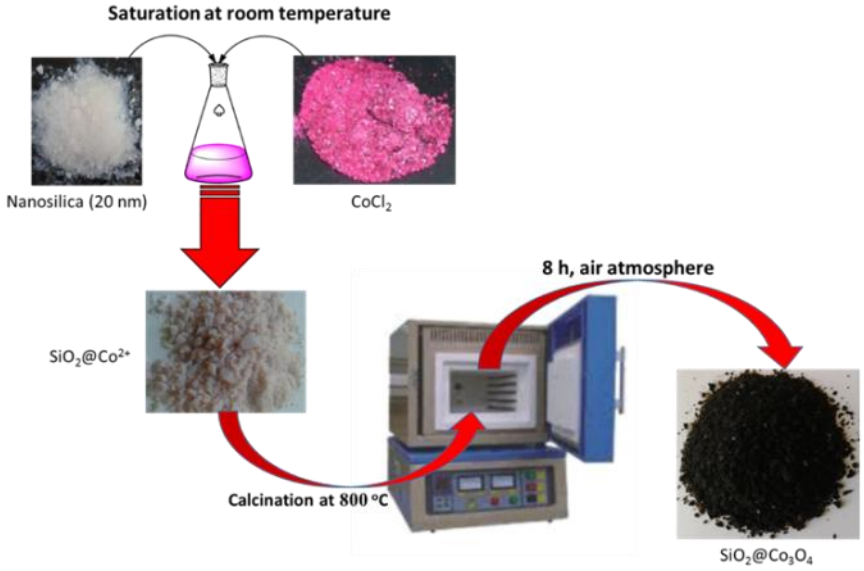

Figure 1. General pathway towards the synthesis of Co_3O_4/SiO_2

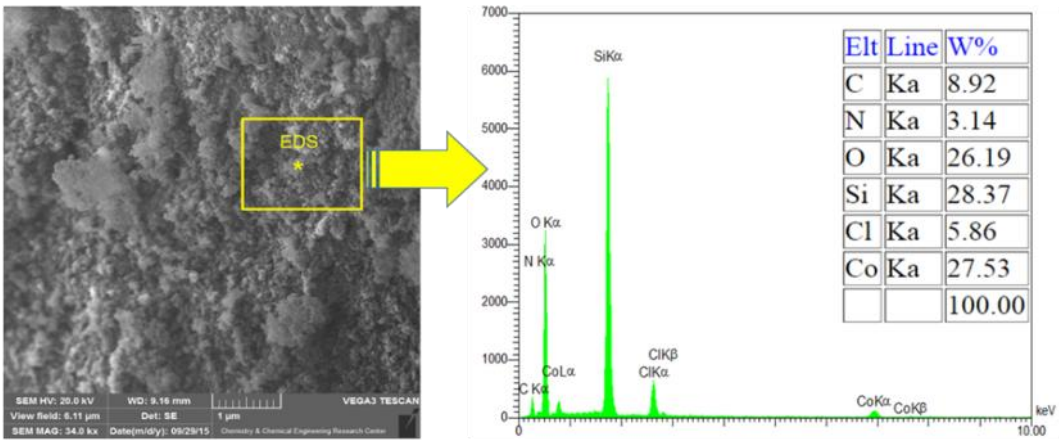

Figure 2. SEM-EDX data of Co_3O_4/SiO_2

degradation was at the maximum amount (Figure 6).

Oxidative degradation of MO was also studied on the temperature raising. It was observed that the raise of temperature has positive effect on the oxidation efficiency of MO. In addition to room temperature, we tested the oxidation reaction at higher temperatures including 35, 45, and 60 °C. This investigation showed that at 60 °C, a rapid degradation of MO in less than 2 min can be observed. Therefore, the temperatures higher than 60 °C was not studied (Figure 7). This study indicated that the degradation of MO is thermally achievable [23].

As oxidative degradation of MO with Co_3O_4/SiO_2 critically depends upon the pH value, we studied the effect of pH values on the degradation of MO. The pH values included 1, 3, 6, 7, 10, and 12. At pH values of 1 and 12, the degradation amount was at its higher amount. The stability of the catalyst is also important that this investigation showed that the catalyst is applicable in a vast pH values. Due to the fact that at temperature of 60 °C, degradation efficiency was remarkable, we studied the effect of pH at this temperature (Figure 8).

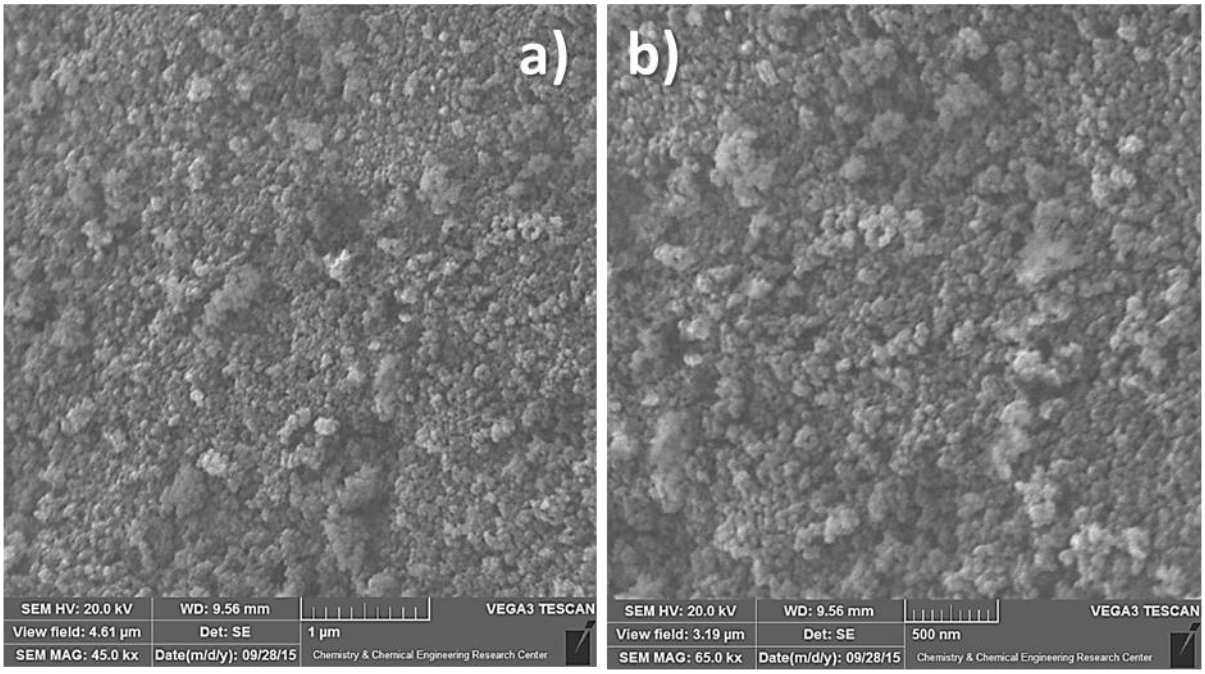

Figure 3. SEM images of Co_3O_4/SiO_2 nanoparticles in two different scales

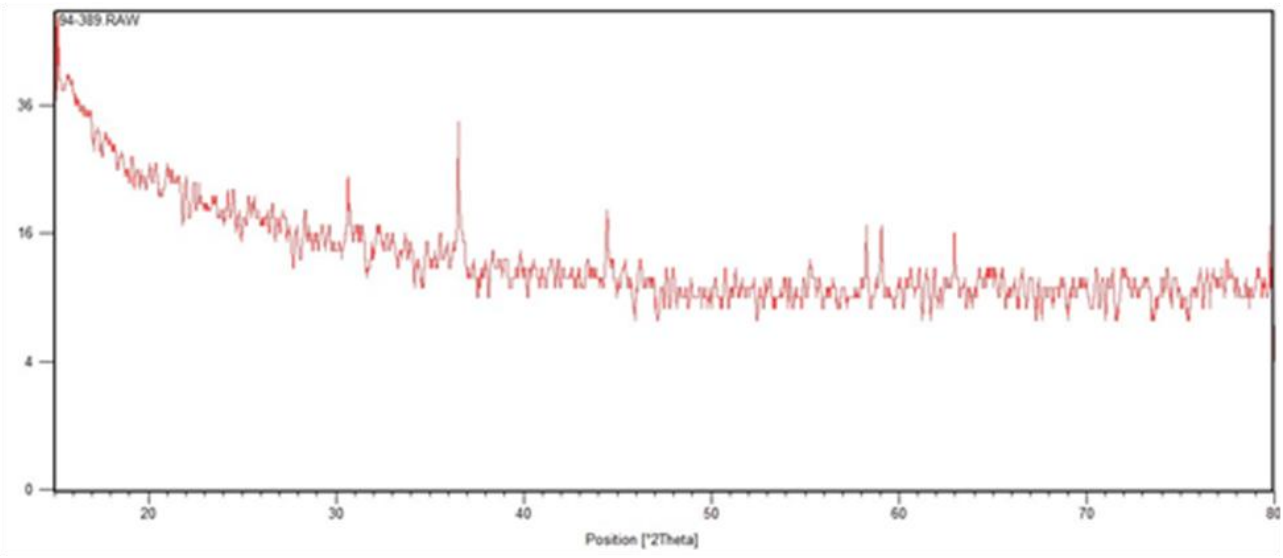

Figure 4. X-ray diffraction pattern of Co_3O_4/SiO_2 (calcined at 800 °C)

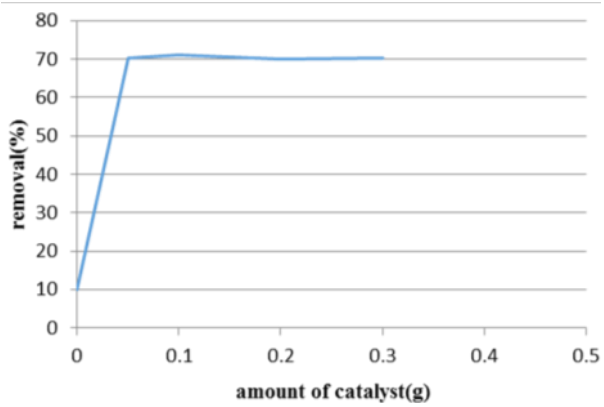

Figure 5. The effect of catalyst amount on the degradation of MO at room temperature in the presence of 0.04 mmol/L PDS during 50 min

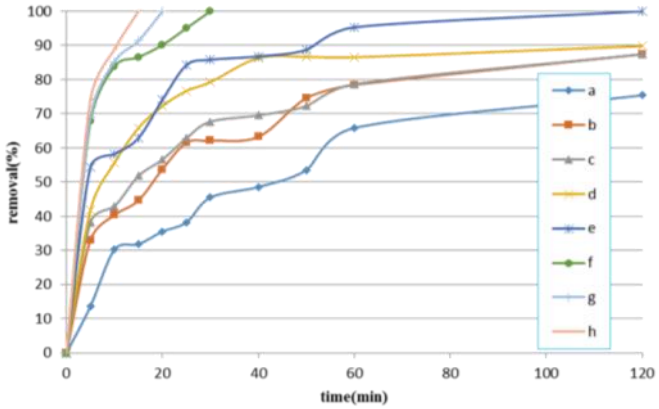

Figure 6. The effect of PDS concentration on the degradation of MO in the presence of 0.05 g Co_3O_4/SiO_2 at room temperature in variable times (a = 0.02 mmol/L, b = 0.04 mmol/L, c = 0.08 mmol/L, d = 0.1 mmol/L, e = 0.2 mmol/L, f = 0.4 mmol/L, g = 0.8 mmol/L, h = 1 mmol/L)

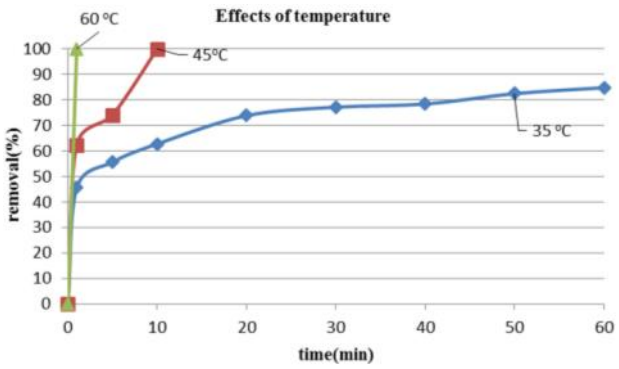

Figure 7. Temperature effect on the removal of MO at neutral pH in the presence of Co_3O_4/SiO_2

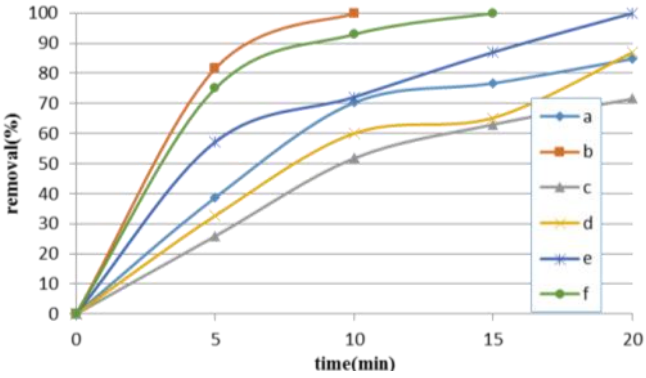

Figure 8. pH effect on the degradation of MO at 60 °C during variable times (pH values include a-f in which a = 10, b = 8, c = 7, d = 6, e = 3, f = 1)

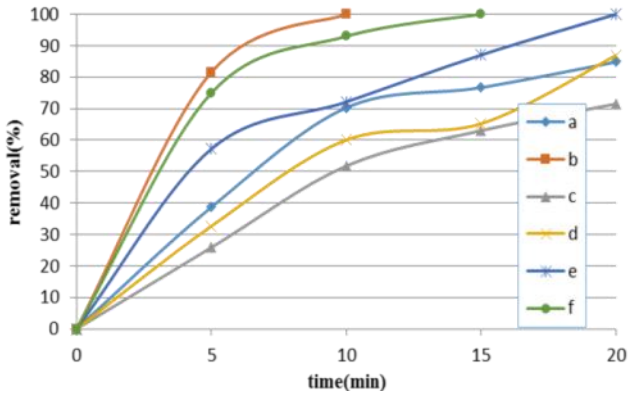

Figure 9. pH effect on the degradation of MO at room temperature in the presence of Co_3O_4/SiO_2 and PDS (pH values include a-f in which a = 10, b = 8, c = 7, d = 6, e = 3, f = 1)

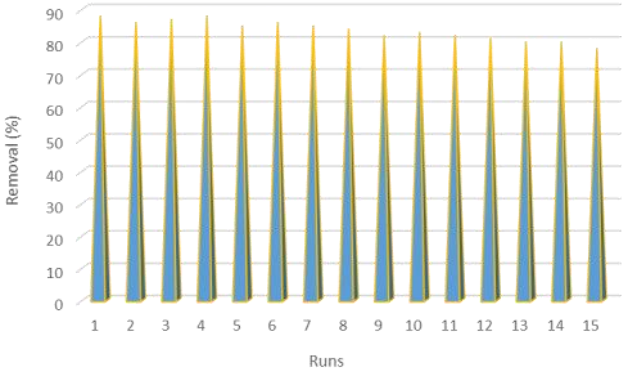

Figure 10. Recyclability of Co_3O_4/SiO_2 over 15 runs at room temperature during 2 h in the presence of 0.04 mM concentration of PDS

On the opposite side, for obtaining a green process, room temperature is the best value for chemical processes. Therefore, we also studied the effect of pH at room temperature (Figure 9).

Stability and recyclability of a heterogeneous catalyst is also a crucial manner which should be taken to account [24-27]. Therefore, we studied the recyclability and stability of the catalyst after 15 runs. During and after 15 runs at room temperature in the presence of PDS, the oxidation efficiency of the catalyst has no meaningful and significant decrease (Figure 10).

4. Conclusions

In summary, a low price and heterogeneous cobalt silica supported cobalt oxide (Co_3O_4/SiO_2) with potential catalytic activity was synthesized by impregnation. The catalyst was studied in the oxidative degradation of MO, and finally was found to be stable, recoverable and efficient catalyst at high temperature and a wide pH range, as well as recyclable at least for 15 consecutive runs. In this degradation process, PDS was the source of sulfate radicals which acted the best. Among adsorption and oxidative degradation, it was proved that the catalyst act as an AOP by coupling with PDS versus adsorption in the removal of MO, as a water pollutant azodye.

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